



Effect of the compact Ti layer on the efficiency of dye-sensitized solar cells assembled using stainless steel sheets

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ABSTRACT

Titanium films have been deposited on stainless steel metal sheets using dc magnetron sputtering technique at different substrate temperatures. The structure of the titanium films strongly depend on the substrate temperature. The titanium film deposited at the substrate temperature lower than 300 °C has a loose flat sheet grains structure and the titanium film prepared at the substrate temperature higher than 500 °C has a dense nubby grains structure. The DSSC assembled using stainless steel sheet coated with titanium film deposited at high substrate temperature has a low charge transfer resistance in the TiO₂/Ti interface and results in a high conversion efficiency. The DSSC assembled using stainless steel sheet coated with titanium film deposited at temperature higher than 500 °C has higher conversion efficiency than that assembled using titanium metal sheet as the substrate. The maximum conversion efficiency, 2.26% is obtained for DSSC assembled using stainless steel sheet coated with titanium film deposited at 700 °C substrate temperature, which is about 70% of the conversion efficiency of the FTO reference cell used in this study.

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1. Introduction

The way we produce and use energy today is not sustainable. Firstly, our main fossil fuel sources – oil, coal and gas – are finite natural resources, and we are depleting them at a rapid rate. Secondly, energy production and use, particularly of fossil fuels, have a number of environmental impacts including air pollution, greenhouse gas emissions and adverse impacts on ecosystems. A fully sustainable renewable power supply is the only way we can secure energy for all and avoid environmental catastrophe. The sun provides an effectively unlimited supply of energy that we can use to generate electricity and heat. The solar energy that reaches the Earth's surface is the largest carbon-free energy source, which could be harvested with photovoltaic or photogalvanic devices. Although the silicon-based solar cells are still dominating the photovoltaic market, several alternatives to Si-based solar cells have become available toward substantially reducing the cost of production. Dye-sensitized solar cells (DSSC) are an alternative to silicon devices as they can be cost-effective, light-weight, portable and flexible.

Since the prototype of a DSSC was reported in 1991 by Gratzel and his coworker [1], it has aroused intense interest owing to its low cost, simple preparation procedure, and benign effect on the environment compared with traditional photovoltaic devices. Recently, a certified photoelectric conversion efficiency of 11% has been achieved [2]. However, the traditional DSSC have an inherent disadvantage of using glass as a substrate material, which makes the cells unsuitable for certain applications except for the high material cost. The fabrication of light-weight, flexible and low-cost DSSC using roll-to-roll mass production can be realized by replacing the glass substrate with polymer or metal foil substrates. Indium-doped tin oxide coated polyethyleneterephthalate (ITO-PET) and polyethylenenaphthalate (ITO-PEN) are the most used conductive polymer substrate. However, their low temperature tolerance needs an alternative deposition or post-treatment technique for the electrode materials, compared with those have been used for glass substrate. As the maximum temperature these polymer substrates can withstand is about 150 °C, the most used colloidal method for preparing the TiO₂ photoelectrode is not suitable for these polymer substrates because it needs to be sintered at 450–500 °C in order to make high quality interconnection between the TiO₂ nanoparticles and with the substrate. Although many studies have attempted to alleviate the problem by introducing new methods to prepare nanoporous TiO₂ photoelectrodes on conducting polymer

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substrates at low temperature [3–8] and a maximum conversion efficiency of 7.6% has been achieved [9,10], a convenient and efficient approach has yet to be proposed.

Metal foil is an alternative substrate material for flexible DSSC. The use of metal foil substrates in flexible DSSC has been studied actively in the past few years mainly because of their endurance of high temperature processing used in TiO_2 photoelectrode preparation [11–18]. The most used metal substrate materials are titanium and stainless steel (SS). The advantage of titanium is its high stability, it cannot be corroded in iodine-based electrode. However, its price is much higher than SS. The SS is cheap, but the stability is not very high. To reduce the cost and improve the stability, it is convenient to deposit a thin protecting layer on a cheap substrate, for instance, SS. The use of different protecting layers, such as SiO_x , ITO, dense TiO_2 on the SS substrate has been reported [11,17,18]. In the present work, the titanium protecting layer has been deposited on the SS by dc sputtering technique at different substrate temperatures. The influence of the substrate temperature on the structure property of these titanium layers and on efficiency of the DSSC assembled using them have been studied. A comparison of a SS substrate system to a conventional FTO glass substrate system has been made.

2. Experimental

The SS sheets used in the experiments were commercial 304 SS with a thickness of 0.2 mm. The SS sheets were first washed using detergent, and then cleaned in a detergent solution, ethanol and acetone separately using an ultrasonic bath for 15 min in each step. The cleaned SS sheets were then transferred to the vacuum chamber and coated with titanium layer using dc magnetron sputtering technique. The sputtering target was titanium metal disk with a diameter of 60 mm and a purity of 99.99%. Before the depositions, the vacuum chamber was pumping down to 3×10^{-3} Pa. And then the argon gas was introduced into the chamber by mass flow controller. The sputtering pressure was set at 0.7 Pa. The sputtering current and the cathode potential were kept at 0.48 A and 0.44 kV, separately. The substrate temperature was varied from room temperature (RT) to 700 °C. The deposition time was 60 min. The thickness of these titanium layers was about 1000 nm measured by SEM. A mesoporous TiO_2 electrode was prepared by traditional doctor-blading technique. In detail, a thin layer TiO_2 paste was coated on Ti sheet. Then the TiO_2 film was sintered at 200 °C for 15 min. Repeats the process above mentioned two times and a 3 layers of TiO_2 film was obtained. After sintered at 500 °C for 30 min, the mesoporous nanocrystalline TiO_2 film was completely fabricated. The thickness of the nanocrystalline TiO_2 film was about 12–13 μm . For comparison study, the same process was not only applied for titanium metal sheet, but also for Ti-coated SS and FTO glass substrates. These TiO_2 electrodes were sensitized with N719 ($\text{Ru(II)L}_2(\text{NCS})_2:2\text{TBA}$, where $\text{L}=2,2'$ -bipyridyl-4,4'-dicarboxylic acid) dye by soaking them in an ethanol solution of N719 dye (0.5 mM) for 12 h at room temperature. The counter electrode was FTO glass coated with Pt and the electrolyte contains of 0.06 M of LiI, 0.6 M 1-propyl-3-methylimidazolium iodide, 0.03 M I_2 , 0.5 M 4-*tert*-butyl pyridine, and 0.1 M guanidinium thiocyanate in acetonitrile.

Surface morphologies of the titanium films prepared at different substrate temperatures were characterized by scanning electron microscopy (SEM, FEI HITACHI 15 S-4800). The XRD experiments were carried out with an automatic X-ray powder diffractometer (D/Max 2400, RIGAKU). Photocurrent–voltage performance of the DSSC was conducted under simulated AM 1.5 illumination ($I=100 \text{ mW cm}^{-2}$, Solar Light Co., INC., USA) with a Keithley digital source meter (Keithley 2601, USA). Cells with an active area

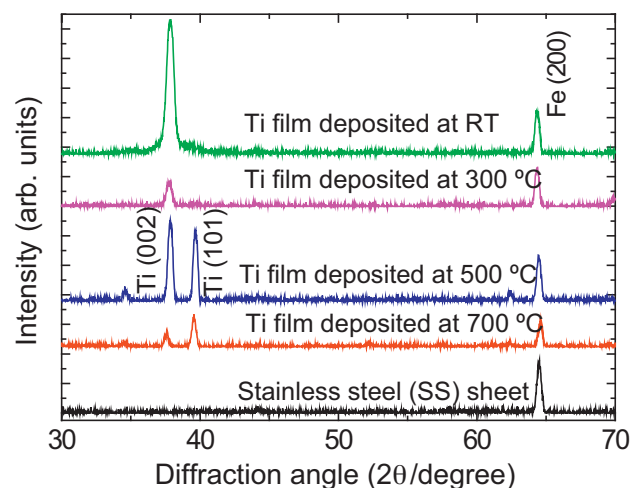


Fig. 1. XRD patterns of titanium layers deposited at different substrate temperatures.

of 0.25 cm^2 were tested. The EIS experiment was characterized in two-electrode system using a computer-controlled potentiostat (ZeniumZahner, Germany) in darkness. The measured frequency ranged from 10^{-1} to 10^6 Hz, the bias was -0.75 V , and the ac amplitude was set to 10 mV.

3. Results and discussion

Figure 1 shows the XRD patterns of the Ti films deposited at different substrate temperatures on SS sheets. For comparison, the XRD pattern of bare SS substrate is also given in Fig. 1. It can be observed that the Ti films deposited at substrate temperature lower than 300 °C show a strong orientation along the (002) direction (PDF card file 44-1294). When the substrate temperature is higher than 500 °C, the (101) diffraction peak appears. This (101) orientation dominates the growth direction as the substrate temperature is 700 °C. The intensity ratio of the $I(101)/I(002)$ has been calculated and shown in Fig. 2. It can be seen that this ratio has a small increase as the substrate temperature is increased from RT to 300 °C. However, the ratio shows a very quick increase with the substrate temperature when it is higher than 300 °C. It indicates that the growth direction tends to be along the (101) direction when the substrate temperature is higher than 300 °C. The mean grain size along the (002) direction has been estimated from Scherrer's formula. The results have been shown in Fig. 2. The grain size increases linearly from 15 to 27 nm as the substrate temperature is

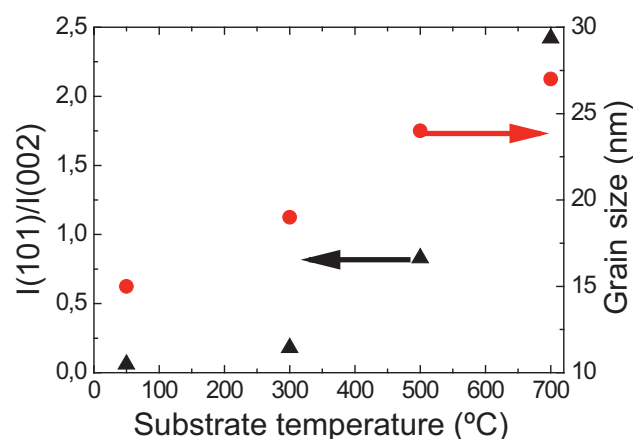


Fig. 2. Peak intensity ratio and grain size as a function of the substrate temperature.

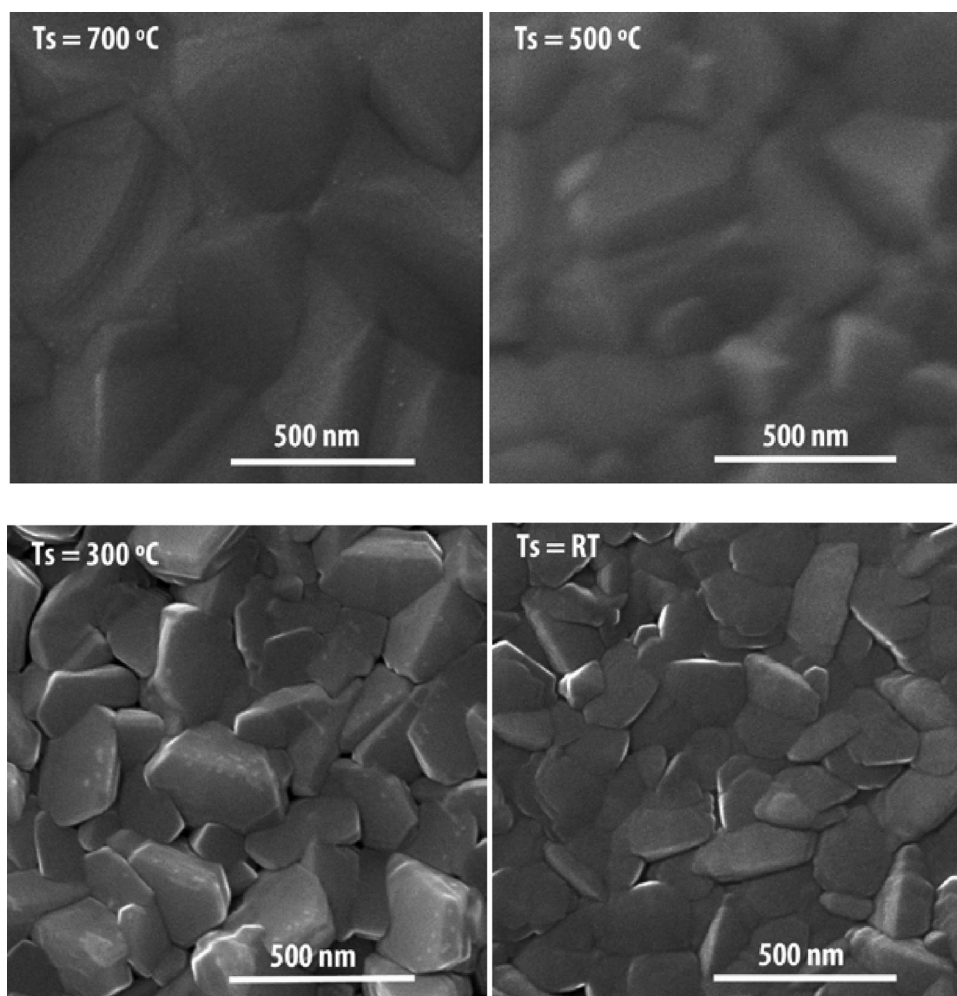


Fig. 3. SEM images of the surface morphology of titanium layers deposited at different substrate temperatures.

increased from RT to 700 °C. That indicates an improvement of the crystallization at high substrate temperature.

The surface morphology of the Ti films deposited at different substrate temperatures on SS substrate was studied by SEM and the results are shown in Fig. 3. At low substrate temperature (lower than 300 °C), the flat sheet grains are loosely packed together. It will form titanium films with a porous structure as it can be seen in Fig. 3. When the substrate temperature is higher than 500 °C, these flat sheet grains change into the nubby grains and the films become relative dense compared with films grown at the temperature lower than 300 °C. This densification is necessary to avoid the corrosion of the SS substrate by electrolyte. It also can be seen from Fig. 3 that the grain size in the sample surface increases as the substrate temperature is increased. Both the increase of the grain size and the densification of the film indicate the improvement of the crystallization of the titanium films at high substrate temperature. The microstructure of sputtered metal films is usually classified by structure-zone models [19]. Microstructures in zone 1 ($T_s/T_m < 0.3$, where T_s is the substrate temperature and T_m melting point of the deposited material) consisted of tapered columns which are separated by voided boundaries. Zone 2 ($0.3 < T_s/T_m < 0.5$) microstructures consisted of columnar grains separated by dense intercrystalline boundaries. Zone 3 ($0.5 < T_s/T_m < 1$) microstructures consisted of more equiaxed grains. For titanium metal, the melting point is about 1660 °C. When the substrate temperature is lower than 300 °C, T_s/T_m is less than 0.3. According to the Thornton structure-zone model, the

deposited films should have tapered columns structure. However, the structure shown in Fig. 3 does not agree with the model. It shows the flat sheet grains with voids between them. When the substrate temperature is increased from 500 °C to 700 °C, the values of T_s/T_m locate in zone 2. Again, no columnar grains separated by dense intercrystalline boundaries structure have been observed. Instead of that, the equiaxed grains have been observed. Although the Thornton structure model cannot be applied directly to these titanium films prepared by dc magnetron sputtering technique, the general statement of the original Thornton model is maintained: increasing the substrate temperature leads to a more compact and dense film structure.

Figure 4 shows the photocurrent density as a function of voltage of DSSCs assembled using SS coated with titanium films deposited at different temperatures as the substrates. For comparison, the results of the DSSC assembled using titanium sheet and FTO glass as the substrates have also been given in Fig. 4. The corresponding photovoltaic parameters of these fresh cells (short-circuit current density, J_{sc} ; open-circuit voltage, V_{oc} ; fill factor, FF and conversion efficiency, η) are listed in Table 1 (The accuracies of the measurements for V_{oc} and J_{sc} are in order of 10^{-3} V and 10^{-3} mA/cm², respectively). From Table 1 it can be seen that the photocurrent density increases as the substrate temperature is increased. It means that the high deposition temperature of titanium film is favorable for increasing the photocurrent density. The photocurrent density J_{sc} depends on the charge injection and collection. Charge injection efficiency is determined by several factors such as

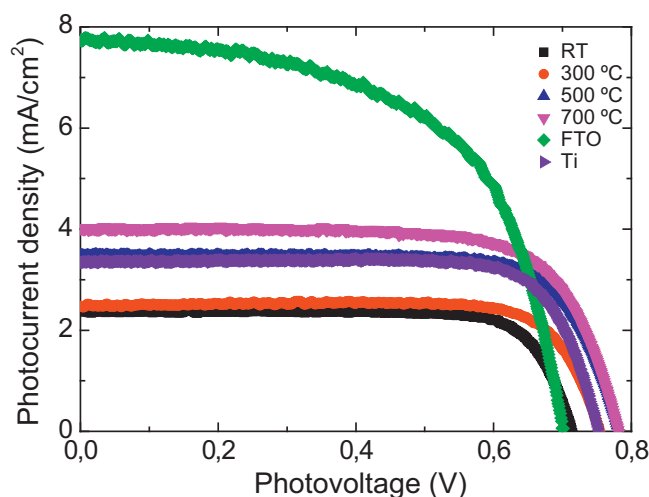


Fig. 4. Photocurrent–voltage curves of the devices based on different substrates.

potential difference between the conduction band edge of TiO_2 and lowest unoccupied molecular orbital of the adsorbed dyes, acceptor density in TiO_2 , and spatial distance between the surface of TiO_2 and the dye. As these DSSCs are assembled using the same process, the only difference is the substrate, the charge injection efficiency should not have any difference for them. Therefore the difference of the J_{sc} must come from the difference of the charge collection efficiency. Although electron diffusion length is a key point for the charge collection efficiency, it does not dominate the variation of the J_{sc} in these DSSCs as the TiO_2 photoelectrodes are made by the same process. The difference of the J_{sc} should come from the difference of the interface between the conducting sheet and TiO_2 . The DSSC assembled using the titanium film deposited at the temperature higher than 500°C on SS has higher charge collection efficiency than that using titanium metal sheet has. This phenomenon may be related with the structure of the titanium film deposited at different substrate temperatures. As it can be seen from Fig. 3 that the titanium films prepared at the substrate temperature lower than 300°C consisted of separated flat sheet grains with voids between them. These voids may result in the loss of the electrons and decrease the charge collection efficiency. When the temperature is higher than 500°C , the voids between the grains disappear, the electrons which reach the conducting layer will be extracted to external load without any loss and result in an increase of the photocurrent density. The origin of photovoltage has not yet been understood. Gregg et al. have suggested that V_{oc} is most likely related with the difference between the Fermi level of semiconductor electrode and redox potential [20]. Our results do not agree well with this suggestion. As the TiO_2 photoelectrode and the electrolyte are the same for all DSSCs, the difference between the Fermi level of semiconductor electrode and redox potential should not have any difference. So the V_{oc} should be the same for all DSSC. However, the V_{oc} is different for different substrates as it can be seen from Table 1. Again it can be seen that the high deposition temperature of titanium film is favorable for the V_{oc} . However, high deposition temperature

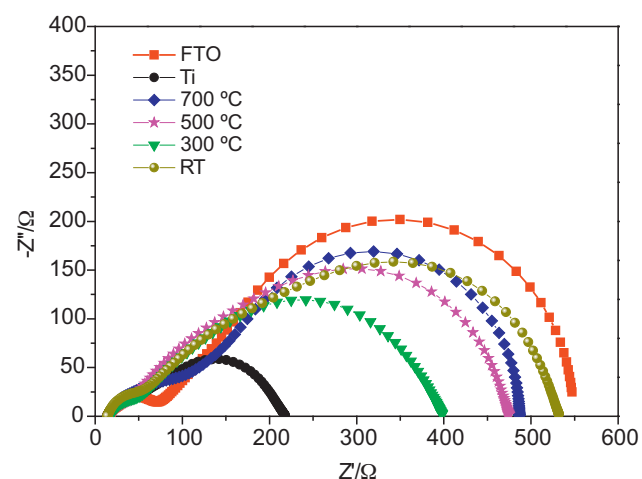


Fig. 5. Nyquist plots of the DSSC assembled with different substrates.

of titanium film is not favorable for the FF. For comparison, the parameters of the DSSC assembled with FTO glass substrate are also given in Table 1. It can be seen that the photocurrent is much higher than the DSSC assembled with titanium metal and SS coated by titanium film substrates. However, the FTO based DSC has the lowest FF. This may indicate the presence of large resistive losses at the electrode-substrate junction as the electrical resistance of FTO substrate is an order of magnitude higher than titanium coated SS substrates. It means FTO substrate has lower charge collection efficiency than titanium. The DSSC assembled using FTO substrate has highest conversion efficiency, this could be ascribed to the large charge recombination for FTO-free based DSSCs. The DSSC assembled with SS coated by titanium film at high substrate temperature shows higher conversion efficiency than that assembled using titanium metal sheet. The efficiency of the DSSC assembled with SS coated by titanium film at 700°C has reached about 70% of the efficiency of the DSSC assembled with FTO glass substrate.

To compare the interfacial charge transfer resistance, electrochemical impedance spectroscopy (EIS) was measured. Figure 5 shows typical Nyquist plots of the DSSC assembled with different substrates. A suggested equivalent circuit representing the DSSC is shown in Figure 6. The intercept on the real axis corresponds to the series resistance (R_s) where the phase is zero. It represents the resistance of the conductive materials in the DSSC with contributions from the SS substrate, TiO_2 photoanode, current collector and resistivity of the electrolyte [21]. Besides, there are three semicircles, from left to right, the left one can be ascribed to counter electrode/electrolyte interface consisted of the charge transfer resistance (R_{ct} (CE)) and the capacitance C_{μ} (CE); the middle one can be ascribed to photoanode/electrolyte interface consisted of the charge transfer resistance (R_{ct} (AE)) and the capacitance C_{μ} (AE); the right one can be ascribe to the Nernst diffusion impedance (Z_N). The EIS parameters for the equivalent circuit of the DSSC are also listed in Table 1. No clear correlation between the series resistance R_s and the conversion efficiency has been found in this work.

Table 1
Photovoltaic and EIS parameters of the DSSC based on different substrates.

	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)	R_s/Ω	R_{ct} (CE)/ Ω	R_{ct} (AE)/ Ω	Z_N/Ω
FTO	7.74	0.70	0.58	3.15	16.8	24.3	23.3	482.6
Ti sheet	3.34	0.75	0.79	1.98	13.3	24.9	94.6	84.9
SS + Ti film deposited at 700°C	4.01	0.78	0.72	2.26	14.8	24.2	45.0	402.6
SS + Ti film deposited at 500°C	3.47	0.78	0.75	2.04	15.4	25.6	206.8	227.2
SS + Ti film deposited at 300°C	2.47	0.75	0.79	1.48	17.3	25.9	220.9	133.9
SS + Ti film deposited at RT	2.36	0.71	0.79	1.33	13.8	25.4	261.3	231.6

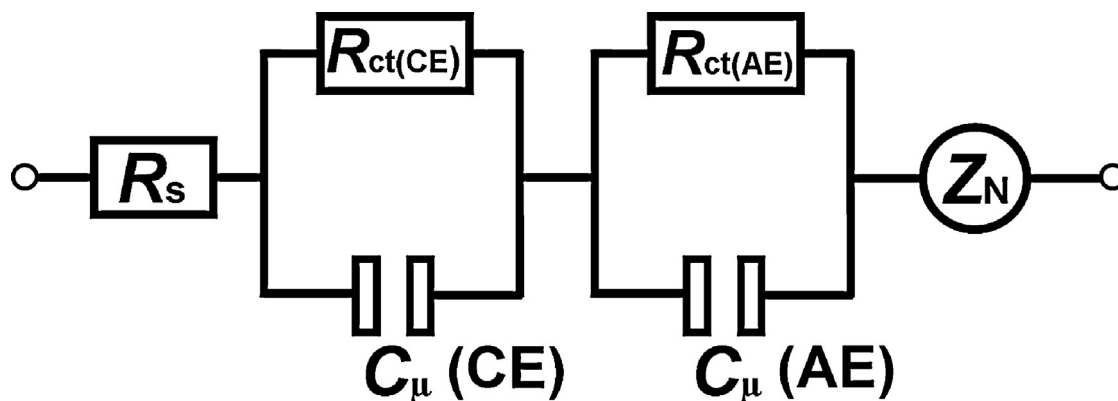


Fig. 6. Suggested equivalent circuit of the DSSC. R_s , series resistance, R_{ct} (CE), charge transfer resistance in the counter electrode/electrolyte interface; R_{ct} (AE), charge transfer resistance in the photoanode/electrolyte interface. Z_N , Nernst diffusion resistance.

And the values of the R_{ct} (CE) are almost the same for all DSCs as shown in Table 1. It can be said that the conversion efficiency is related with R_{ct} (AE). It can be seen that for the SS coated with titanium, as the substrate temperature is increased from the room temperature to 700 °C, the value of R_{ct} (AE) decreased from 261.3 to 45.0 Ω , and the conversion efficiency is enhanced from 1.33% to 2.06%. However, comparing to FTO, the best SS still shows inferior behavior, evidenced by the difference on R_{ct} (AE) and conversion efficiency. The only difference for these DSSCs is the substrate as all the DSSCs should have the same photoelectrode/electrolyte and counter electrode/electrolyte interfaces. Therefore, it is suggested that the difference of this charge transfer resistance results from the TiO_2/Ti interface. According to the EIS data, there may exist a large charge recombination in the TiO_2/Ti interface, and this is adverse to change collection efficiency. Fortunately, improve the substrate temperature can lower the charge transfer resistance and inhibit charge recombination in the TiO_2/Ti interface, resulting in a high photocurrent density and then a high efficiency which is agreeable with efficiency measurement.

4. Conclusions

DSSCs have been assembled using titanium metal sheet, titanium film coated flexible SS sheets and FTO as substrates. Titanium film deposited at high substrate temperature (higher than 500 °C) shows a very dense structure. The DSSC assembled using SS sheet coated by titanium film prepared at high substrate temperature has a low charge transfer resistance in the TiO_2/Ti interface and leads to a high conversion efficiency. The conversion efficiency of the DSSC assembled using SS sheet coated by titanium film at 700 °C is 2.26%, which is 70% of the FTO reference cell (3.15%).

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